New aromatic azo compounds: syntheses and liquid-crystalline properties

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The chemical syntheses of 12 new azo dyes are reported. The optically active compounds were prepared by the Mitsunobu reaction, amide formation, and esterification with optically active alcohols or acids. Several new compounds showed liquid-crystalline properties, and their phase transition behavior was investigated.

Key words: liquid crystals, azo dyes, optically active, phase transition.

The development of new electro-optical liquid crystal devices stimulated interest in the chemistry of dyes.[1—5] Recently,[5—8] a phenomenon of photoinduced optical anisotropy was discovered in the Langmuir films of azo-dyes. The illumination of the Langmuir films with polarized light induces an optical axis perpendicular to the polarization plane. The mechanism of this process was studied both for the Langmuir films[6] and for free standing films.[9] In addition, it was found[10] that it is possible to control the pretilt angle of the director on substrates covered with a photoactive polymer. This parameter essentially determines the switching time constant of LC-displays. Molecules with large conjugated π-systems are very promising active materials for investigations of nonlinear phenomena.[1,2,11] The dye molecules are used as side-chain moieties in liquid-crystalline polymers, which are currently a subject of intensive research. The liquid-crystalline properties of dyes are of great importance for non-linear applications.[11]

From a basic point of view, azo dyes belong to the simplest physical systems in which light illumination induces *cis—trans* isomerization and a local change in the structure of the liquid-crystalline phases. These changes can be responsible for the variation of the optical constants of the media, which may be used in various electro-optical applications. The function of liquid crystal devices is based on the controlled reorientation of the director in the electric field. Anisotropic effects in dyes are more pronounced when a dye exhibits mesogenic properties. In such cases a better orientation of dye molecules on the substrates and a strong orientational optical nonlinearity can be expected.

The goal of the paper was to develop generally applicable and improved synthetic procedures for the diazo coupling reaction aimed at affording products of high purity required for liquid crystal research. In addition, the methods for introducing chirality at different positions of the extended molecules were explored.

New azo dyes capable of formation of liquid crystalline phases were synthesized, and preliminary investigation of their liquid-crystalline properties was undertaken.

Results and Discussion

Syntheses of azo dyes. Several methods are known for the synthesis of azo dyes.[12—15] The most common and frequently used method is the azo coupling reaction. However, only strongly nucleophilic electron-rich aromatic or heteroaromatic compounds such as phenols and amines can be coupled with diazonium salts to yield azo compounds.[13] To maintain satisfactory reaction rates of the coupling it is necessary to control carefully the optimum pH value at which both the diazonium salt and the electron-rich coupling component are most active. The solvent system also has to be appropriately adapted to allow the reaction of the water-soluble diazonium salt and poorly soluble coupling components. The solubility and reactivity can also be influenced by the counter-ion of the diazonium salt, temperature, concentration, mode of addition, and the stirring speed of the mostly heterogeneous reaction mixtures.

We now describe the optimized conditions for the preparation (Scheme 1) of twelve azo dyes **4a—l** with different substituents both in the diazonium ions **2** (generated from amines **1**) and coupling components **3**. The examples were primarily selected with respect to their possible properties as liquid crystals, which show photoinduced orientation effects, a phenomenon discovered by Weigert and Nakashima.[16] Requisite structural elements for the occurence of these effects are the presence of azo and amino groups. In addition, different substituents both in the diazonium ion (**2** in Scheme 1: R = alkyl, cyano, carboxylic, ester, amido group) and coupling partner (**3**: R′ = primary and secondary amino, hydroxy, ether group) cover a broad range of chemical and physical properties (transverse permanent dipoles, strong longitudinal dipoles, *etc.*). These representative examples include the attachment of chiral subunits in the proximity of the permanent dipoles. Thus, the care-

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fully elaborated conditions may be generally useful for the preparation of related compounds to be used in liquid crystal research.

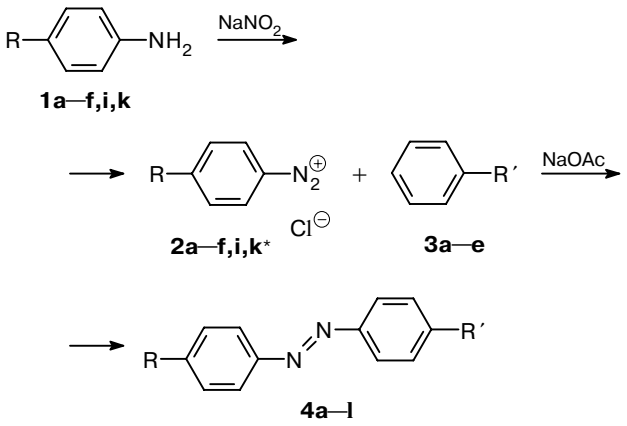
Diazonium salts **2** were prepared from amines **1** in aqueous solution by the addition of 2.5—3 equiv. of HCl and 1 equiv. of $NaNO_2$ (introduced as a 2.5 *M* solution) in a temperature range of 0—5 °C (~5 h of the reaction time, see Experimental). In the case of 4-aminobenzonitrile (**1d**) it was advantageous to prepare the more stable 4-cyanobenzenediazonium tetrafluoroborate (**2d**) using a described procedure.[17]

For the subsequent diazo coupling reaction, the cold diazonium salt solution was first buffered by AcONa at pH 6 for coupling with amines or at pH 8 for coupling with phenols. Hydrophobic amines, which are poorly soluble in water, such as *N*-(*n*-nonyl)aniline (**3a**), diphenylamine (**3b**), and *N,N*-di(*n*-hexyl)aniline (**3c**) were (partially) dissolved in ethanol, and buffered diazonium salt solution was added under stirring. The stirring speed in the heterogeneous reaction mixture has to be adjusted in such a way that a film of the amine may be formed on the aqueous layer. If the stirring speed is too high, the formation of trombic amine particles prevents the required close contact with the aqueous solution of diazonium salt. To obtain the coupling products of high purity, it was essential to ensure a complete conversion of the diazonium salt. The completeness of the reaction was checked by the reaction of a sample of the reaction mixture with α-naphthylamine solution, indicating the presence of diazonium salts by a color reaction.

Differrent reaction sequences were applied in the syntheses of the chiral enantiomerically pure azo dyes. Chiral acid **4e** was prepared in racemic form by coupling of the diazonium salt **2e** with the racemic secondary amine **3e** (Scheme 2). In the case of chiral ester **4f**, enantiomerically pure amino ester **1f** [18] was diazotized with nitrite and coupled with amine **3a** (see Scheme 2). An alternative pathway to prepare **4f** by esterification of acid **4g** (prepared by coupling of **2e** with **3a**) with (*S*)-butan-2-ol (**5**) failed under a variety of conditions. However, **4g** can be esterified with alcohol (*S*)-**5** under Mitsunobu conditions[19] with inversion of configuration of the alcoholic component. In this way *R*-enantiomer **4h** of *S*-ester **4f** was prepared (see Scheme 2). The optical purity of esters **4f** and **4h** was proved by the measurement of optical rotation and, in addition, by HPLC on chiral columns, indicating a complete inversion of configuration during the Mitsunobu reaction.[19]

Carbamate **4j** containing the fragment of optically active alcohol (*S*)-**5** was prepared *via* the Williamson ether synthesis of phenol **4i** with 1-nonyl bromide. Phenol **4i** could be prepared by coupling of the diazonium salt **2i** derived from the corresponding amine **1i** [18] with phenol **3i**. Finally, chiral azo dyes also can be obtained by esterification with chiral acids. This was exemplified by the reaction of the acid chloride **6** [20] (*ee* > 98.5%) derived from (*S*)-2-chloro-3-methylbutanoic acid with phenol **4k** to afford the enantiomerically pure α-chloro ester **4l** (see Scheme 2). The phenol **4k** was prepared in the usual way by coupling of diazonium salt **2k** with amine **3a**.

Scheme 1



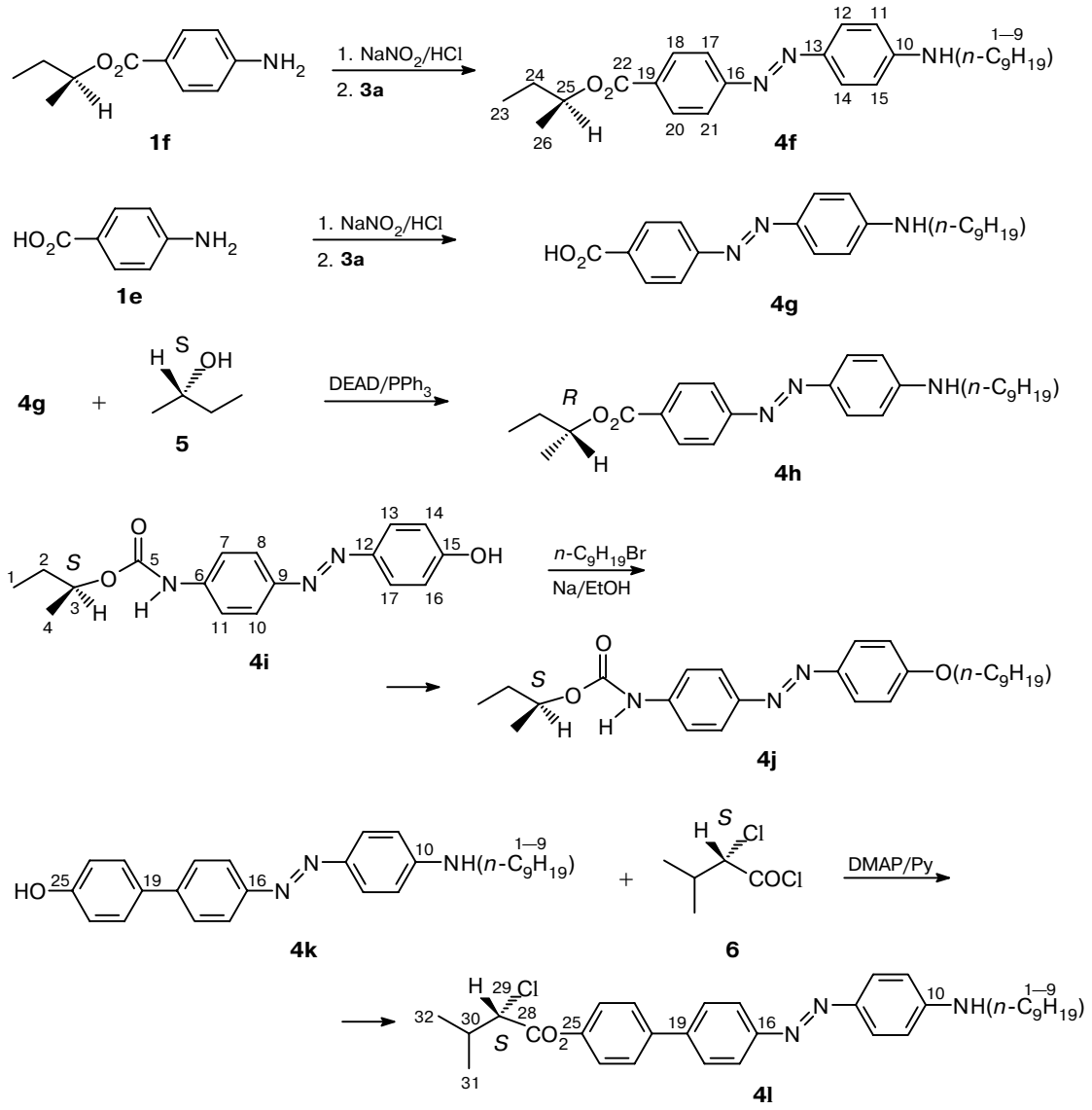
	R	R′
1a—4a	Et	HN(*n*-C_9H_{19})
1b—4b	4-$Pr^nC_6H_4$	HNPh
1c—4c	(*E*)-4-$O_2NC_6H_4CH{=}CH$	N(*n*-C_6H_{13})$_2$
1d—4d*	NC	N(*n*-C_5H_{11})
1e—4e	HO_2C	$NHBu^s$
1f, 2f, 4f	O_2C, H	HN(*n*-C_9H_{19})
4g	HO_2C	HN(*n*-C_9H_{19})
4h	O_2C, H	HN(*n*-C_9H_{19})
1i—4i	O_2CNH, H	OH
4j	O_2CNH, H	O(*n*-C_9H_{19})
1k, 2k, 4k	HO	HN(*n*-C_9H_{19})
4l	H, Cl, CO_2	HN(*n*-C_9H_{19})

* Compound **2d** is tetraflouroborate.

Liquid-crystalline properties. Optical investigation showed that among the prepared compounds only azo dyes **4a—d,e** possess mesophases. The temperatures of the corresponding phase transitions and the types of the mesophases were determined (Table 1). The DSC data (see Table 1) confirmed the results obtained by the optical method. The enthalpies of the phase transitions are also presented in Table 1.

The smectic A phase is characterized by a fan-shaped or polygonal texture, which are the two possible

Scheme 2



modifications of the focal conic texture. The fan-shaped texture, as observed for azo compound **4a** (Fig. 1), showed typical disclination lines forming hyperbolas lying in the plane of the preparation. This texture preferentially appeared in thin specimens. In contrast, the polygonal texture occurring in thicker layers form focal ellipses lying in the planes of the upper and lower glasses. The transition enthalpies are typical of the crystalline—smectic A and smectic A—isotropic phase transitions.

Compound **4b** revealed the crystalline—nematic phase transition at 147 °C. The nematic-isotropic phase transition presumably occured at temperatures >240 °C and was not observable. At temperatures closely below 240 °C we observed the decomposition of the material in the nematic phase. In some cases, we were able to register the nematic—isotropic phase transition below 240 °C for partially decomposed **4b**. In such cases we also observed the formation of the nematic phase on cooling (Fig. 2). The nematic marbled texture observed at 147 °C consisted of several areas with different molecular orientations. These regions with nearly homogeneous orientations were indicated by the nearly constant interference colors within individual areas. All phase boundaries of the solid phases preserved. They were strongly pinned at the glass surface and appeared unaltered even after heating above the clearing point of the partially decomposed **4b**. The boundaries disappeared only after heating for longer times at temperatures considerably higher than the clearing point. This texture was observed in thin specimens.

Compound **4c** showed the crystalline—smectic C transition, which can be identified both in the polarizing microscope and by DSC measurements. These findings

Table 1. Temperatures (T/°C) and enthalpies (ΔH/kJ mol^{-1}) of the phase transitions for azo compounds **4a**—**d**,**l**

Phase transition	**4a**		**4b**		**4c**		**4d**		**4l**	
	T	ΔH	T	ΔH	T	ΔH	T	ΔH	T	ΔH
K—S_A	57.5	7.055	—	—	—	—	—	—	—	—
S_A—I	75.0	1.568	—	—	—	—	—	—	—	—
K—N	—	—	147.0	1.163	—	—	—	—	188.2	1.832
K—S_C	—	—	—	—	169.7	9.434	—	—	—	—
S_C—I	—	—	—	—	180.0	1.887	—	—	—	—
K—S_E	—	—	—	—	—	—	132.2	1.446	—	—
S_E—S_A	—	—	—	—	—	—	143.4	7.664	—	—
S_A—N	—	—	—	—	—	—	230.2	2.382	—	—

corresponded with the observations, which were described earlier.[11] The smectic C phase appearing at 169.7 °C showed a broken fan-shaped texture. The characteristic branches of hyperbolas indicated this texture. However, in contrast to the smectic A phase of azo compound **4a**, more discontinuities occurred in the smectic C phase.

The textures of azo dye **4d** have been described earlier.[21] The smectic E phase was observed at 132.2 °C. The mosaic smectic E texture is characterized by differently colored optically homogeneous regions with irregular boundaries. The optical homogeneity of the regions indicated the orientation of the director. The smectic A phase characterized by a typical polygonal texture occurred at 143.4 °C. The nematic state at 230.2 °C displayed a typical "schlieren" texture. The optical characteristics of this texture were dark brushes with irregular curved shapes. The chiral azo dye **4l** showed a cholesteric phase with typical "oily streaks". The cholesteric—isotropic transition occurred possibly at temperatures >240 °C and could not be observed due to decomposition of the compound.

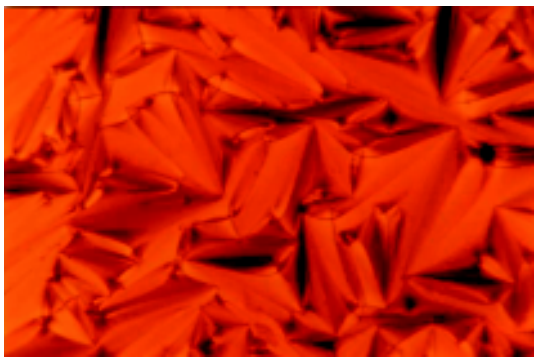


Fig. 1. Fan-shaped texture of smectic A of **4a**, crossed polarizers, 100 × magnification, 57.5 °C.

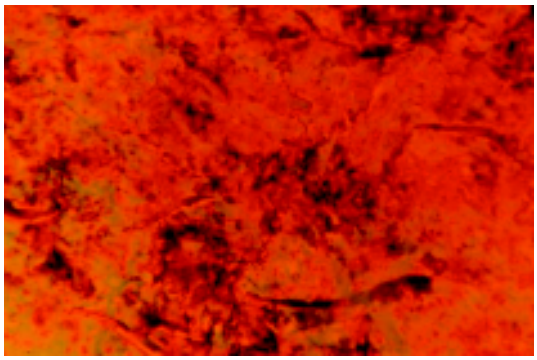


Fig. 2. Nematic marbled texture of **4b**, crossed polarizers, 100 × magnification, 147 °C.

Experimental

For instrumentation and general methods see Ref. 22. Silica gel 60 (0.040—0.063 mm, Machery & Nagel) was used for chromatography. The transition temperatures and mesophase identifications were determined by a LEITZ SM-LUX polarizing microscope equipped with a Mettler heating stage in a temperature range of 20—240 °C. In all experiments the heating rate was 2 °C min^{-1}. The differential scanning calorimetry was carried out in a dry nitrogen flow, using a Perkin—Elmer DSC-2 calorimeter connected with a data station at heating and cooling rates of 10 °C min^{-1}. Reagents from Fluka were used in syntheses. Solvents were purified by standard procedures.[23]

Test 1 (for $NaNO_2$). A sample of the reaction solution (0.1 mL) was treated with a 1% solution of sulfanilic acid in 30% AcOH (0.1 mL) and subsequently with a 3% solution of 1-naphthylamine in 30% AcOH (0.1 mL). The presence of free sodium nitrite was indicated by a violet color and verified by TLC comparison with authentic coupling product of sulfanilic acid with 1-naphthylamine (CH_2Cl_2 as the eluent).

Test 2 (for unreacted diazonium salt). A sample of the reaction mixture (0.1 mL) was mixed with a 3% solution of 1-naphthylamine in 30% AcOH (0.1 mL). The presence of unreacted diazonium salt was indicated by the appearance of the violet color of the naphthylamine coupling product.

***N*-[4-(4-Ethylphenylazo)phenyl]-*N*-nonylamine (4a).** In a three-necked 25 mL vessel equipped with internal thermometer, dropping funnel, and magnetical stirrer, 4-ethylaniline (**1a**) (0.55 g, 4.6 mmol) was dissolved in a mixture of water (8 mL) and conc. HCl (1.2 mL). The solution was cooled to 0 °C and treated dropwise with a solution of $NaNO_2$ (0.32 g, 4.6 mmol) in water (1 mL) taking care that the temperature did not exceed 5 °C during the diazotation procedure. After 3 h, a 0.1 mL sample was withdrawn and tested for the presence of nitrite (Test 1). The test indicated that the nitrite was completely consumed after 5 h of stirring. The mixture was then buffered to pH 6 by addition of AcONa (1.5 g). The cold solution was transferred into a dropping funnel and added

dropwise at 0—5 °C to a solution of *N*-(*n*-nonyl)aniline (**3a**)[24] (1.0 g, 4.6 mmol) in EtOH (4.8 mL) taking care that the temperature did not exceed 10 °C during the addition, and the mixture was stirred for another 48 h at 8 °C. The test indicated the absence of unreacted diazonium salt (Test 2). The reaction was then quenched by addition of a 10% aqueous solution of Na_2CO_3 (6 mL). The red-brown precipitate was filtered off, washed with water (40 mL), and dried under reduced pressure. The residue was dissolved in the minimum amount of CH_2Cl_2 (~3 mL), chromatographed on neutral Al_2O_3 (elution with hexane—CH_2Cl_2, 2 : 2.4) and crystallized from CH_2Cl_2—cyclohexane to afford yellow crystals of **4a** (0.72 g, 45%), m.p. 75 °C. Found (%): C, 78.71; H, 9.56; N, 11.85. $C_{23}H_{33}N_3$. Calculated (%): C, 78.58; H, 9.46; N, 11.95. IR (KBr), ν/cm^{-1}: 3428 (NH); 2930, 2849, 1604, 1518, 1340, 1138, 839, 824. UV (hexane), λ_{max}/nm (log ε): 245.5 (4.05), 381 (4.49). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.94 (t, 3 H, H(15), J = 6.9 Hz); 1.32 (m, 15 H, H(1), H(17), H(18), H(19), H(20), H(21), H(22)); 1.67 (m, 2 H, H(16)); 2.75 (q, 2 H, H(2), J = 7.6 Hz); 3.23 (t, 2 H, H(15), J = 6.9 Hz); 4.12 (s, 1 H, NH); 6.68 (m, 2 H, H(10), H(12)); 7.34 (m, 2 H, H(4), H(8)); 7.81—7.89 (m, 4 H, H(5), H(7), H(9), H(13)). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 15.9 (q, C(23)); 23.1 (q, C(1)); 27.5 (t); 29.2 (t); 29.7 (t); 29.9 (t); 30.0 (t); 32.3 (t, C(2)); 44.1 (t, C(15)); 112.5 (d, C(10), C(12)); 122.7 (d, C(4), C(8)); 125.5 (d, C(9), C(13)); 128.8 (d, C(5), C(7)); 146.5 (s, C(11)); 151.3 (s, C(6), C(14)). MS (70 eV, 90 °C), m/z (I_{rel} (%)): 352 [M$^+$ + H] (30), 351 [M]$^+$ (100), 238 (32), 218 [M$^+$ − PhNHC$_9$H$_{19}$] (34), 106 (42), 105 [M$^+$ − PhC$_2$H$_5$] (32).

***N*-Phenyl-[4-(4′-propylbiphenyl-4-ylazo)phenyl]amine (4b).** 4-Amino-4′-(*n*-propyl)biphenyl (**1b**)[25] (0.8 g, 3.8 mmol) was diazotized as described for **4a** (4 h) and then coupled with diphenylamine (**3b**) (0.64 g, 3.8 mmol) in EtOH (4 mL) (24 h) to afford **4b** (1.12 g, 61%), m.p. 230 °C. Found (%): C, 82.65; H, 6.31; N, 10.58. $C_{27}H_{25}N_3$. Calculated (%): C, 82.83; H, 6.44; N, 10.73. IR (KBr), ν/cm^{-1}: 3393 (NH); 2950, 1588, 1518, 1300, 1233, 1140, 839, 747. UV (hexane), λ_{max}/nm (log ε): 254 (4.20), 315.5 (4.00), 324.5 (4.00), 397 (4.55). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.03 (t, 3 H, H(1), J = 7.3 Hz); 1.72 (m, 2 H, H(2)); 2.69 (t, 2 H, H(3), J = 7.6 Hz); 6.09 (s, 1 H, NH); 7.07—7.44 (m, 9 H, H(5), H(9), H(17), H(19), H(22), H(23), H(24), H(25), H(26)); 7.64 (d, 2 H, H(6), H(8), $J_{6,5}$ = 8.0 Hz); 7.76 (d, 2 H, H(10), H(14), $J_{10,11}$ = 8.5 Hz); 7.94 (d, 2 H, H(16), H(20), $J_{16,17}$ = 8.8 Hz); 7.98 (d, 2 H, H(11), H(13), $J_{11,10}$ = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 14.3 (q, C(1)); 24.9 (t, C(2)); 38.2 (t, C(3)); 116.2 (d, C(22), C(26)); 120.4 (d, C(18), C(20)); 123.2 (d, C(24)); 123.4 (d, C(5), C(9)); 125.3 (d, C(23), C(25)); 127.4 (d, C(6), C(8)); 127.9 (d, C(10), C(14)); 129.4 (d, C(17), C(21)); 130.0 (d, C(11), C(13)); 138.1 (s, C(27)); 141.7 (s, C(19)); 147.1 (s, C(21)); 152.3 (s, C(12)). MS (70 eV, 150 °C), m/z (I_{rel} (%)): 392 [M$^+$ + H] (30), 391 [M]$^+$ (100), 168 [—PhNHPh] (86), 167 [PhNHPhH] (40).

***N*,*N*-Dihexyl-*N*-(4-{4-[2-(4-nitrophenyl)vinyl]phenylazo}phenyl)amine (4c).** 4-Amino-4′-nitrostilbene (**1c**)[26] (1.5 g, 6.3 mmol) was reacted with $NaNO_2$ (0.43 g, 6.25 mmol) as described for **4a** (4h) and coupled with dihexylaniline (**3c**)[27] (1.63 g, 6.3 mmol) in EtOH (5.5 mL) to yield ruby-red platelets of **4c** (2.05 g, 64%), m.p. 180 °C. Found (%): C, 75.12; H, 8.02; N, 10.95. $C_{32}H_{40}N_4O_2$. Calculated (%): C, 74.97; H, 7.86; N, 10.93. IR (KBr), ν/cm^{-1}: 2924, 2859, 1597, 1509, 1393, 1364, 1134, 849. UV (hexane), λ_{max}/nm (log ε): 454.5 (4.65); 348.0 (4.33); 262.5 (4.12). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.96 (t, 6 H, H(26), H(32), J = 6.7 Hz); 1.39 (s, 12 H, H(23), H(24), H(25), H(29), H(30), H(31)); 1.66 (d, 4 H, H(22), H(28), J = 7.1 Hz); 3.40 (t, 4 H, H(21), H(27), J = 7.4 Hz); 6.73 (d, 2 H, H(17), H(19), $J_{17,16}$ = 9.1 Hz); 7.19 (d, 1 H, H(7), $J_{7,8}$ = 16.4 Hz); 7.33 (d, 1 H, H(8), $J_{8,7}$ = 16.0 Hz); 7.66 (d, 4 H, H(3), H(5), H(10), H(14), $J_{3,2}$ = 8.7 Hz); 7.89 (d, 4 H, H(11), H(13), H(16), H(20), $J_{11,10}$ = 8.5 Hz); 8.25 (d, 2 H, H(2), H(6), $J_{11,10}$ = 8.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 14.5 (q, C(26), C(32)); 23.1 (t, C(25), C(31)); 27.2 (t); 27.8 (t); 32.1 (t, C(22), C(28)); 51.7 (t, C(21), C(27)); 111.5 (d, C(17), C(19)); 123.2 (d); 124.6 (d); 125.9 (d); 127.0 (d); 127.3 (d); 128.2 (d); 133.2 (d, C(2), C(6)); 137.2 (s, C(18)); 143.6 (s, C(9)); 144.2 (s, C(4)); 147.1 (s, C(1)); 151.2 (s, C(15)); 153.8 (s, C(12)). MS (70 eV, 120 °C), m/z (I_{rel} (%)): 514 [M$^+$ + H] (30), 513 [M$^+$] (70), 441 (100), 371 (66), 234 (70), 219 (100).

4-Cyanobenzenediazonium tetrafluoroborate (2d). A solution of 4-aminobenzonitrile (**1d**) (3.0 g, 25.4 mmol) in 40% HBF_4 (11.2 mL) was treated at −5 °C with a solution of $NaNO_2$ (1.73 g, 25.4 mmol) in water (3.5 mL) cooled to 0 °C (5 h). The yellow-brownish precipitate was then filtered off, washed with cold HBF_4 (3 mL), 95% EtOH (5 mL), and then with Et_2O (5 mL) to afford the salt **2d** (4.1 g, 84%, *cf.* Ref. 17).

4-[4-(4-Pentylpiperazin-1-yl)phenylazo]benzonitrile (4d). To a solution of 1-(*n*-pentyl)-4-phenylpiperazine (**3d**)[21] (2.0 g, 8.62 mmol) in 1 *M* HCl (165 mL) was added with cooling to 5 °C and stirring the solid diazonium salt **2d** (1.87 g, 8.6 mmol). The red solution was stirred for 24 h and the pH was then adjusted to pH 10 by addition of 10 *M* NaOH solution. The precipitate was filtered off and purified as described for **4a** to afford **4d** (2.6 g, 83%), m.p. 230 °C (*cf.* Ref. 20, m.p. 252 °C). Found (%): C, 73.23; H, 7.62; N, 19.48. $C_{22}H_{27}N_5$. Calculated (%): C, 73.09; H, 7.58; N, 19.38. IR (KBr), ν/cm^{-1}: 2980, 2845, 2226 (CN); 1599, 1507, 1383, 1237, 1146, 852. UV (hexane), λ_{max}/nm (log ε): 223.5 (3.99); 271.0 (4.13); 418.5 (4.52). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.96 (t, 3 H, H(22), J = 6.8 Hz); 1.35—1.65 (m, 6 H, H(19), H(20), H(21)); 2.44 (t, 2 H, H(18), J = 7.4 Hz); 2.64 (t, 4 H, H(15), H(16), J = 5.1 Hz); 3.46 (t, 4 H, H(14), H(17), J = 5.0 Hz); 6.99 (d, 2 H, H(10), H(12), $J_{10,9}$ = 9.1 Hz); 7.78 (d, 2 H, H(3), H(7), $J_{3,4}$ = 8.5 Hz); 7.93 (d, 2 H, H(9), H(13), $J_{9,10}$ = 9.0 Hz); 7.94 (d, 2 H, H(4), H(6), $J_{4,3}$ = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 14.5 (q, C(22)); 23.0 (t, C(21)); 27.0 (t, C(20)); 30.2 (t, C(19)); 47.9 (t, C(18)); 53.3 (t, C(15), C(16)); 59.1 (t, H(14), C(17)); 112.8 (s, C(2)); 114.4 (d, C(10), C(12)); 119.3 (s, C(1)); 123.3 (d, C(3), C(7)); 125.9 (d, C(9), C(13)); 133.5 (d, C(4), C(6)); 145.4 (s, C(11)); 154.3 (s, C(8)); 155.7 (s, C(5)). MS (70 eV, 120 °C), m/z (I_{rel} (%)): 361 [M$^+$] (38), 304 [M$^+$ − (CH$_2$)$_3$Me] (100).

4-[4-(*sec*-Butylamino)phenylazo]benzoic acid (4e). 4-Aminobenzoic acid (**1e**) (2 g, 14.6 mmol) was diazotized as described for **4a** and coupled with butylaniline **2e**[28] (2.17 g, 14.6 mmol) in EtOH (15 mL). The reaction was quenched by addition of a 30% Na_2CO_3 solution (30 mL) to yield red **4e** after column chromatography on silica gel (elution with CH_2Cl_2) (2.71 g, 62%), m.p. 201 °C. Found (%): C, 68.49; H, 6.61; N, 14.07. $C_{17}H_{19}N_3O_2$. Calculated (%): C, 68.67; H, 6.44; N, 14.13. IR (KBr), ν/cm^{-1}: 3399 (NH); 2963, 1686 (C=O); 1597, 1514, 1393, 1291, 1132, 862, 829, 775. UV (CH_2Cl_2), λ_{max}/nm (log ε): 274.0 (4.05); 424 (4.48). ^{1}H NMR (200 MHz, CD_3OD), δ: 0.99 (t, 3 H, H(1), J = 7.4 Hz); 1.33 (d, 3 H, H(4), J = 6.5 Hz); 1.71 (m, 2 H, H(2)); 3.95 (m, 1 H, H(3)), 7.14 (d, 2 H, H(6), H(10), $J_{6,7}$ = 9.3 Hz); 7.78 (d, 2 H, H(13), H(15), $J_{13,12}$ = 8.7 Hz); 7.99 (m, 2 H, H(7), H(8)); 8.08 (m, 2 H, H(12), H(16)). ^{13}C NMR (50 MHz, CD_3OD), δ: 10.6 (q, C(1)); 19.7 (q, C(4)); 30.0 (t, C(3)); 54.5 (d, C(3)); 112.5 (d, C(6), C(10)); 122.1 (d, C(13), C(15)); 126.3 (d, C(7), C(9)); 131.0 (d, C(12), C(16)); 145.6 (s, C(5)); 148.5 (s, C(8), C(11)); 168.8 (s, C(17)). MS (70 eV, 105 °C), m/z (I_{rel} (%)):

297 [M^+] (64), 268 [$M^+ - C_2H_5$] (100), 148 [$PhNHC_4H_9$] (40), 119 (58), 92 (24), 65 (20), 44 (28).

4-[4-(*n*-Nonylamino)phenylazo]benzoic acid (*S*)-*sec*-butyl ester (4f). 4-Aminobenzoic acid (*S*)-*sec*-butyl ester (**1f**)[18] (0.5 g, 2.59 mmol) was diazotized in the usual way (see **4a**, water (4.5 mL), conc. HCl (0.7 mL), $NaNO_2$ (0.178 g, 2.59 mmol), 4 h stirring). The coupling was performed with *N*-(*n*-nonyl)aniline (**3a**) (0.57 g, 2.6 mmol) in EtOH—water (1 : 1) (3 mL) for 36 h. The mixture was then extracted with CH_2Cl_2 (2 × 20 mL), the red organic solution was washed with water (30 mL), dried (Na_2SO_4), filtered, and the solvent was removed at reduced pressure to afford **4f** after crystallization from CH_2Cl_2—cyclohexane (0.76 g, 69%), m.p. 83 °C, $[\alpha]_D^{20}$ +24.1 (*c* 1.10, CH_2Cl_2). Found (%): C, 73.80; H, 8.95; N, 9.97. $C_{26}H_{37}N_3O_3$. Calculated (%): C, 73.72; H, 8.80; N, 9.92. IR (KBr), ν/cm^{-1}: 3386 (NH); 2924, 2853, 1696, 1597, 1534, 1240, 1132, 827, 775. UV (hexane), λ_{max}/nm (log ε): 266.5 (4.08), 399.5 (4.54). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.90 (t, 3 H, H(1), *J* = 6.9 Hz); 1.01 (t, 3 H, H(23), *J* = 7.4 Hz); 1.29 (s, 12 H, H(2), H(3), H(4), H(5), H(6), H(7)); 1.37 (d, 3 H, H(26), *J* = 6.3 Hz); 1.73 (m, 4 H, H(7), H(24), *J* = 6.3 Hz); 3.21 (m, 2 H, H(9)); 4.26 (s, 1 H, NH); 5.13 (s, 1 H, H(25)); 6.65 (d, 2 H, H(11), H(15), $J_{11,12}$ = 8.9 Hz); 7.87 (d, 4 H, H(12), H(14), H(17), H(21), $J_{18,17}$ = 8.7 Hz); 8.16 (d, 2 H, H(18), H(20), $J_{12,11}$ = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 9.6 (q, C(1)); 13.9 (q, C(23)); 19.4 (q, C(26)); 22.5 (t, C(2)); 26.9 (t); 28.8 (t); 29.1 (t); 29.2 (t); 29.2 (t); 29.3 (t); 31.7 (t, C(24)); 43.4 (t, C(9)); 72.8 (d, C(25)); 111.9 (d, C(11), C(15)); 121.7 (d, C(18), C(20)); 125.6 (s, C(19)); 130.3 (d, C(12), C(14), C(17), C(21)); 144.4 (s, C(10)); 151.5 (s, C(13)); 155.6 (s, C(16)); 165.8 (s, C(22)). MS (70 eV, 100 °C), *m/z* (I_{rel} (%)): 423 [M^+] (100), 254 (22), 218 [$M^+ - PhNHC_9H_{19}$] (48), 106 (40), 105 (20), 69 (15).

4-[4-(*n*-Nonylamino)phenylazo]benzoic acid (4g). 4-Aminobenzoic acid (**1e**) (1.5 g, 11 mmol) was diazotized in the usual way (water (18.6 mL), conc. HCl (2.8 mL), $NaNO_2$ (0.756 g, 11 mmol), 4 h). Coupling with *N*-(*n*-nonyl)aniline (**3a**) (2.4 g, 11 mmol) (24 h at 8 °C, quenching with a 10% Na_2CO_3 solution (60 mL)) and chromatography on silica gel (elution with acetone) afforded **4g** (3.27 g, 81%), m.p. 82 °C. Found (%): C, 70.80; H, 7.70; N, 11.20. $C_{22}H_{29}N_3O_2$. Calculated (%): C, 71.90; H, 7.95; N, 11.43. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.93 (t, 3 H, H(1), *J* = 6.8 Hz); 1.33 (m, 12 H, H(2), H(3), H(4), H(5), H(6), H(7)); 1.80 (s, 2 H, H(8)); 4.34 (t, 2 H, H(9), *J* = 7.6 Hz); 7.22 (t, 1 H, NH); 7.51 (m, 4 H, H(11), H(12), H(14), H(15)); 7.69 (d, 2 H, H(17), H(21), $J_{17,18}$ = 8.6 Hz); 8.20 (d, 2 H, H(18), H(20), $J_{18,17}$ = 8.5 Hz); 11.90 (s, 1 H, OH). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 14.5 (q, C(1)); 23.1 (t, C(2)); 26.3 (t); 27.6 (t); 29.7 (t); 29.9 (t); 32.3 (t); 117.7 (d, C(11), C(15)); 121.6 (d, C(12), C(14)); 124.5 (d, C(17), C(21)); 129.7 (d, C(18), C(20)); 131.8 (s, C(19)); 144.6 (s, C(10)); 155.2 (s, C(13), C(16)); 172.5 (s, C(22)).

4-[4-(*n*-Nonylamino)phenylazo]benzoic acid (*R*)-*sec*-butyl ester (4h). The benzoic acid **4g** (1.00 g, 2.7 mmol), (*S*)-butan-2-ol (**5**) (0.20 g, 2.7 mmol) and PPh_3 (0.71 g, 2.7 mmol) were dissolved in dry THF (3 mL). Diethylazodicarboxylate (DEAD) (0.47 g, 2.7 mmol) was then added dropwise to the solution and the mixture was stirred at 20 °C for 16 h. The solvent was evaporated at reduced pressure, the mixture was redissolved in CH_2Cl_2 (3 mL) and chromatographed on silica gel (elution with CH_2Cl_2) to yield the optically active ester **4h** (0.23 g, 20%), m.p. 83 °C, $[\alpha]_D^{20}$ –23.9 (*c* 1.08, CH_2Cl_2). Found (%): C, 73.58; H, 8.97; N, 10.10. $C_{26}H_{37}N_3O_3$. Calculated (%): C, 73.72; H, 8.80; N, 9.92. IR (KBr), ν/cm^{-1}: 3386 (NH); 2924, 2853, 1696, 1597, 1534, 1387, 1358, 1275, 1240, 1130, 1092, 862, 826, 775. UV (hexane), λ_{max}/nm (log ε): 267 (4.07), 394.5 (4.57). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.91 (t, 3 H, H(1), *J* = 6.8 Hz); 1.01 (t, 3 H, H(23), *J* = 7.4 Hz); 1.29 (s, 12 H, H(2), H(3), H(4), H(5), H(6), H(7)); 1.34 (d, 3 H, H(26), *J* = 6.2 Hz); 1.73 (m, 4 H, H(8), H(24)); 3.21 (m, 2 H, H(9)); 4.26 (s, 1 H, NH); 5.13 (m, 1 H, H(25)); 6.65 (d, 2 H, H(11), H(15), $J_{11,12}$ = 8.9 Hz); 7.87 (d, 4 H, H(12), H(14), H(17), H(21), $J_{18,17}$ = 8.7 Hz); 8.16 (d, 2 H, H(18), H(20), $J_{12,11}$ = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 9.6 (q, C(1)); 13.9 (q, C(23)); 19.4 (q, C(26)); 22.5 (t, C(2)); 26.9 (t); 28.8 (t); 29.1 (t); 29.2 (t); 29.2 (t); 29.3 (t); 31.7 (t, C(24)); 43.4 (t, C(9)); 72.8 (d, C(25)); 111.9 (d, C(11), C(15)); 121.7 (d, C(18), C(20)); 125.6 (s, C(19)); 130.3 (d, C(12), C(14), C(17), C(21)); 144.4 (s, C(10)); 151.5 (s, C(13)); 155.6 (s, C(16)); 165.8 (s, C(22)). MS (70 eV, 100 °C), *m/z* (I_{rel} (%)): 424 [M^+ + H] (20), 218 [$PhNHC_9H_{19}$] (20), 205 [$M^+ - PhNHC_9H_{19}$] (22), 177 [$PhCO_2C_4H_9$] (100), 121 (52), 106 (48), 104 (22).

[4-(4-Hydroxyphenylazo)phenyl]carbamic acid (*S*)-*sec*-butyl ester (4i). 4-Aminophenylcarbamic acid (*S*)-*sec*-butyl ester (**1i**)[18] (0.91 g, 4.4 mmol) was diazotized in the usual way (see **4a**, water (6 mL), conc. HCl (0.9 mL), $NaNO_2$ (0.30 g, 4.4 mmol), 4h). The coupling reaction was performed by addition of this solution to a mixture of phenol **3i** (0.41 g, 4.4 mmol) in 20% aqueous NaOH solution (5 mL) and stirring for 24 h at 8 °C. The azo dye was precipitated by addition of 1 *M* HCl (14 mL). Preparative TLC on silica gel (4 mm, elution with CH_2Cl_2) afforded **4i** (0.99 g, 72%), m.p. 144 °C, $[\alpha]_D^{20}$ +14.1 (*c* 1.08, CH_2Cl_2). ^{1}H NMR (300 MHz, acetone-d_6), δ: 0.94 (t, 3 H, H(1), *J* = 7.4 Hz); 1.26 (d, 3 H, H(4), *J* = 6.2 Hz); 1.62 (m, 2 H, H(2)); 4.83 (m, 1 H, H(3)); 7.01 (d, 2 H, H(14), H(16), $J_{14,13}$ = 8.8 Hz); 7.77 (d, 2 H, H(7), H(11), $J_{7,8}$ = 8.8 Hz); 7.85 (t, 4 H, H(8), H(10), H(13), H(17), $J_{13,14}$ = 8.3 Hz); 8.86, 8.99 (both s, 2 H, OH, NH). ^{13}C NMR (75 MHz, acetone-d_6), δ: 9.9 (q, C(1)), 19.9 (q, C(4)); 29.0—30.6 (t, C(2)); 73.4 (d, C(3)); 116.6 (d, C(14), C(16)); 119.1 (d, C(7), C(11)); 124.1 (d, C(13), C(17)); 125.4 (d, C(8), C(10)); 142.6 (s, C(6)); 147.2 (s, C(12)); 148.8 (s, C(9)); 154.1 (s, C(15)); 161.0 (s, C(5)).

4-[4-(*n*-Nonyloxy)phenylazo]phenylcarbamic acid (*S*)-*sec*-butyl ester (4j). A solution of the phenolic azo compound **4i** (0.334 g, 1.1 mmol) in dry EtOH (1.5 mL) was added to a solution of Na (0.025 g, 1.1 mmol) in dry EtOH (4.85 mL) within 30 min and stirring was continued for 20 min. The solution was treated with KI (0.1 g) and 1-bromononane (0.22 g, 1.1 mmol). The mixture was heated for 10 h to 60 °C, Na (0.004 g, 0.17 mmol) and 1-bromononane (0.035 g, 0.17 mmol) were added and the mixture was heated for an additional 4 h. On cooling to 20 °C, a precipitate was formed which was filtered off and dried to afford **4j** (0.251 g, 53%), m.p. 117 °C, $[\alpha]_D^{20}$ +11.5 (*c* 1.08, CH_2Cl_2). Found (%): C, 70.99; H, 8.53; N, 9.49. $C_{26}H_{37}N_3O_3$. Calculated (%): C, 71.03; H, 8.48; N, 9.55. IR (KBr), ν/см$^{-1}$: 3345 (NH), 2938, 2923, 2853, 1705 (C=O), 1609, 1597, 1534, 1505, 1237, 1057, 847. UV (hexane), λ_{max}/nm (log ε): 246.0 (4.18), 356.5 (4.48), 435.0 (3.32). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.90 (t, 3 H, H(1), *J* = 7.2 Hz); 0.97 (t, 3 H, H(23), *J* = 7.4 Hz); 1.30 (m, 13 H, H(2), H(3), H(4), H(5), H(6), H(26)); 1.47 (m, 2 H, H(7)); 1.64 (m, 2 H, H(24)); 1.83 (m, 2 H, H(8)); 4.04 (t, 2 H, H(9), *J* = 6.8 Hz); 4.89 (m, 1 H, H(25)); 6.74 (s, 1 H, NH); 7.00 (d, 2 H, H(11), H(15), $J_{11,12}$ = 9.0 Hz); 7.53 (d, 2 H, H(18), H(20), $J_{18,17}$ = 8.7 Hz); 7.88 (d, 2 H, H(12), H(14), $J_{12,11}$ = 8.9 Hz); 7.89 (d, 2 H, H(17), H(21), $J_{17,18}$ = 8.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 5.3 (q, C(1)); 9.7 (q, C(23)); 15.3 (q, C(26)); 18.3 (t, C(2)); 21.7 (t); 24.6 (т); 24.8 (t); 24.9 (t); 25.0 (t); 25.2 (t); 27.5 (t, C(8)); 31.7 (t, C(24)); 64.0 (t, C(25));

69.3 (t, C(9)); 110.3 (d, C(11), C(15)); 114.0 (d, C(18), C(20)); 119.4 (d, C(12), C(14)); 120.1 (d, C(17), C(21)); 135.8 (s, C(19)); 142.5 (s, C(10)); 144.2 (s, C(13)); 148.7 (s, C(16)); 157.1 (s, C(22)). MS (70 eV, 100 °C), m/z (I_{rel} (%)): 440 [M^+ + H] (30), 439 [M^+] (100), 383 [M^+ + H − C_4H_9] (30), 365 [M^+ − H − OC_4H_9] (38), 234 (22), 219 [$C_9H_{19}OPh$—] (36), 212 (22), 136 [$PhNHCO_2$] (22), 121 (28), 107 (50), 93 (28), 69 (32), 57 (36).

4′-[4-(*n*-Nonylamino)phenylazo]biphenyl-4-ol (4k). 4-Amino-4′-hydroxybiphenyl (**1k**)[29] (1.00 g, 5.4 mmol) was diazotized in the usual way (see **4a**, water (16 mL), conc. HCl (2.3 mL), $NaNO_2$ (0.37 g, 5.4 mmol), 7 h), and coupling was performed with *N*-(*n*-nonyl)aniline (**3a**) (1.19 g, 5.4 mmol), in EtOH (6 mL) (49 h). The dark precipitate was dissolved in CH_2Cl_2 (40 mL) and filtered over a batch of silica gel. The product was further purified by preparative TLC on silica gel (4 mm, elution with CH_2Cl_2) to afford **4k** (0.65 g, 29%), m.p. 147 °C. Found (%): C, 77.36; H, 7.99; N, 9.70. $C_{21}H_{29}N_3O$. Calculated (%): C, 78.04; H, 8.00; N, 10.11. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.93 (t, 3 H, H(1), J = 6.8 Hz); 1.33—1.47 (m, 12 H, H(2), H(3), H(4), H(5), H(6), H(7)); 1.67—1.74 (m, 2 H, H(8)); 3.25 (t, 2 H, H(9), J = 7.0 Hz); 4.17 (s, 1 H, NH); 4.86 (s, 1 H, OH); 6.69 (d, 2 H, H(11), H(15), $J_{11,12}$ = 8.8 Hz); 6.96 (d, 2 H, H(24), H(26), $J_{24,23}$ = 8.5 Hz); 7.59 (d, 2 H, H(23), H(27), $J_{23,24}$ = 8.5 Hz); 7.69 (d, 2 H, H(18), H(20), $J_{18,17}$ = 8.5 Hz); 7.91 (t, 4 H, H(12), H(14), H(17), H(21), $J_{12,11}$ = 8.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 10.4 (q, C(1)); 22.5 (t); 26.5 (t); 28.9 (t); 29.1 (t); 29.2 (t); 29.8 (t); 31.8 (t, C(8)); 43.5 (t, C(9)); 112.5 (d, C(11), C(15)); 116.2 (d, C(24), C(26)); 123.1 (d, C(23), C(27)); 125.7 (d, C(18), C(20)); 127.5 (d, C(12), C(14)); 128.8 (d, C(17), C(21)).

(*S*)-2-Chloro-3-methylbutyric acid 4′-[4-(*n*-nonylamino)phenylazo]biphenyl-4-yl ester (4l). A solution of the azo phenol **4k** (0.25 g, 0.6 mmol) in dry Py (3 mL) was treated with 0.1 g dimethylaminopyridine (DMAP) and (*S*)-2-chloro-3-methylbutyric acid chloride (**6**) (0.10 g, 0.65 mmol), prepared from (*S*)-valine[28]. The mixture was stirred for 14 h at 60 °C, then poured into 1 *M* HCl (10 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The organic phase was washed twice with 1 *M* HCl (10 mL) and once with water (10 mL), dried (Na_2SO_4), filtered, and the solvent was evaporated at reduced pressure. The residue was purified by preparative TLC on silica gel (elution with CH_2Cl_2—hexane, 2 : 1) to afford **4l** (0.180 g, 55%), m.p. 188 °C, $[\alpha]_D^{20}$ +4.9 (*c* 0.94, CH_2Cl_2). Found (%): C, 71.83; H, 7.65; N, 8.02. $C_{32}H_{40}N_3O_2Cl$. Calculated (%): C, 71.95; H, 7.55; N, 7.87. IR (KBr), ν/cm^{-1}: 3405 (NH); 2924, 2855, 1552 (C=O); 1603, 1522, 1140, 833. UV (hexane), λ_{max}/nm (log ε): 235.0 (4.14), 397.5 (4.66). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.91 (t, 3 H, H(1), J = 6.3 Hz); 1.19 (d, 6 H, H(31), H(32), J = 6.7 Hz); 1.30—1.44 (m, 12 H, H(2), H(3), H(4), H(5), H(6), H(7)); 1.62—1.71 (m, 2 H, H(8)); 2.52 (m, 1 H, H(30)); 3.21 (t, 2 H, H(9), J = 7.1 Hz); 4.18 (s, 1 H, NH); 4.38 (d, 1 H, H(29), J = 6.6 Hz); 6.66 (d, 2 H, H(11), H(15), $J_{11,12}$ = 8.9 Hz); 7.22 (d, 2 H, H(24), H(26), $J_{24,23}$ = 8.6 Hz); 7.68 (m, 4 H, H(18), H(20), H(23), H(27)); 7.86 (d, 2 H, H(12), H(14), $J_{12,11}$ = 8.8 Hz); 7.92 (d, 2 H, H(17), H(21), $J_{17,18}$ = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 14.0 (q, C(1)); 18.0 (q); 19.5 (q); 22.5 (t, C(2)); 26.9 (t, C(3)); 29.1 (t); 29.2 (t); 29.2 (t); 29.4 (t); 31.7 (t, C(8)); 32.6 (d, C(30)); 43.4 (t, C(9)); 63.7 (d, C(29)); 111.9 (d, C(11), C(15)); 121.4 (d, C(24), C(26)); 122.6 (d, C(23), C(27)); 125.2 (d, C(18), C(20)); 127.6 (d, C(12), C(14)); 128.1 (d, C(17), C(21)); 138.6 (s, C(22)); 140.7 (s, C(19)); 144.4 (s, C(10)); 149.8 (s, C(25)); 151.0 (s, C(13)); 152.2 (s, C(16)); 167.8 (s, C(28)). MS (70 eV, 175 °C), m/z (I_{rel} (%)): 533 [M^+] (100), 335 (22), 169 (30), 44 [CO_2] (40).

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